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Integration of Multiwalled Carbon Nanotubes in Bulk Heterojunction CdSe/PCPDTBT Hybrid Solar Cells

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Abstract. In this work, the development of solution-processed bulk heterojunction hybrid solar cells based on CdSe quantum dot (QD) and conjugated polymer poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b] dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)], PCPDTBT was performed. The photoactive layer was formed by integrating CdSe QDs onto multiwalled carbon nanotubes (CNTs). A simple method of thiol functionalization in the interface CNTs and CdSe QDs has been investigated. Integration of CNTs enhances long-term performance of solar cells devices. Initial PCE values of about 1.9 % under AM1.5G illumination have been achieved for this hybrid CNT-CdSe photovoltaic device. In addition, the long-term stability of the photovoltaic performance of the devices was investigated and found superior to CdSe QD only based devices. About 84 % of the initial PCE remained after storage in a glove box for one year without any further encapsulation. It is concluded that the improvement is mainly due to a strong binding between thiol functionalized CNTs and CdSe QDs, resulting preservation of the nanomorphology of the hybrid film over time.

Introduction

Solution-processed solar cells based on organic–inorganic hybrid materials have been developed as an alternative route towards low-cost fabrication, high efficiency, light-weight and flexible large-area devices [1]. However, solar cells based on solution-processed hybrid materials reported thus far generally suffer from low device efficiencies and poor long-term stability in air [2]. These problems are caused by limitation in electron conductivity and mobility which are mainly related to the un-optimized nanomorphology of the hybrid photoactive film resulted from the nanophase separation of the donor and acceptor phases during solvent evaporation and annealing of the film. Therefore, the design of a more continuous electron-transport pathway combined with environmental stability should significantly enhance the performance of hybrid solar cells. In this context, carbon-based materials such as carbon nanotubes (CNTs) are ideal organic compounds to be combined with inorganic semiconductor quantum dots (QDs). CNTs possess excellent environmental stability and high charge mobilities, which could be utilized to overcome the low electron mobilities in hybrid solar cells [3, 4]. Hence, a major challenge in hybrid photovoltaic devices could be overcome by simultaneously achieving the goals of high efficiency, solution-processability, and long-term stability. Especially the latter aspect, the device stability has been given relatively little attention so far [5].

There have already been several efforts to incorporate CNTs into solar cells, for example as a hole extraction layer [6, 7], and as charge transport layer or electrode [4, 8]. So far, only a relatively low PCE of 0.7 % has been reported for CNTs incorporated into the active layer of hybrid solar

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cells [9]. The preparation of CNT-QDs hybrid materials is usually based on the simple addition of QDs to CNTs, utilizing solely Van der Waals interactions between QDs and the surface of the CNTs [10]. Nevertheless, this method tends to result in uncontrolled QD loading. Using in-situ synthesis of semiconductor nanoparticles directly on the surface of CNTs might be considered as an alternatives route. However, this route was found to interfere with the QD synthesis leading to non-uniform and polydisperse nanocrystals [11, 12]. In this work, therefore, we apply a simple synthesis method towards thiol-functionalized CNTs recently reported for the thiolation of reduced graphene-oxide [13, 14]. The successful incorporation of a novel hybrid material based on cadmium selenide (CdSe) QDs bound to thiolated CNTs into active layers of hybrid solar cells is reported. This method demonstrates a promising potential path towards air-stable high-performance solution-processed hybrid solar cells.

Experimental Methods

CdSe QD synthesis

The CdSe QDs were synthesized according to the procedure set-up by Yuan et al[15]. First, 2898 mg of HDA (hexadecylamine, 95%, Merck Schuchardt), 3092 mg of TOPO (trioctylphosphine oxide, 99%, Sigma-Aldrich), and 444 mg of Cd-stearate were heated up in a nitrogen atmosphere inside a 25 ml three-neck 300 °C. After reaching 300 °C, 400 ml of a 1 M solution of selenium in TOP (trioctylphosphine, 97%, ABCR) was rapidly injected. The synthesis was continued under vigorous stirring at 1000 rpm and stopped after 30 min.

CNTs Functionalization

Acid functionalization of CNTs were performed according to a procedure reported in the literature [14, 16]. In brief, pristine multiwalled CNTs (Baytubes, Bayer Material Science) were sonicated for 24 hours at 70 °C in a mixture of concentrated HNO_3 and H_2SO_4 with the volume ratio of 3:1. Afterwards, the products were intensively washed with water three times and referred as CNT. For, thiol-functionalization, the acid-treated CNTs subsequently were refluxed with phosphorus pentasulfide (P_4S_{10}) in DMF (dimethylformamide, ≥99.8%, Carl Roth) and heated up to 120 °C in a vacuum for 24 hours [14, 18]. Subsequently, similar washing was utilized, and the products were referred as thiolated carbon nanotubes (TCNT).

CNT–CdSe QD hybrid formation

At this stage, the CNTs products were added to CdSe QDs. Typically, 1.6 mg CdSe QDs, were dissolved in 4.9 ml HA (hexanoic acid) and stirred for 22 min at 110 °C in order to reduce the amounts of organic ligands [17]. Afterwards, double volume (in respect to HA) of methanol was then added to the solution and stirred for another 11 min. Separation of QDs was conducted by centrifuging the dispersion for 1 min at 14.500 rpm. Afterwards, chloroform and methanol with a ratio of 1:3 were added to precipitate the QDs again in order to remove the residual HA. After being recovered by centrifugation, the QDs were finally dispersed in chlorobenzene at a certain concentration. Finally, the CdSe QDs solution was mixed with CNT into the centrifugation tube, resulting in a 400: <1 weight ratio of CdSe QDs: nanocarbon product. This is the optimum ratio which has been published in previous reports[13]. The same procedure is also applied for TCNT-CdSe QDs.

Solar cell manufacturing

Carbon nanotubes–CdSe QD/PCPDTBT hybrid solar cells were fabricated and compared to CdSe QD/PCPDTBT solar cells which served as reference. The devices were manufactured on a structured ≤10 Ωsq ITO substrate (Präzisions Glas & Optik GmbH), that was treated for 5 min with oxygen plasma before Baytron AI4083 PEDOT:PSS from HC Starck was spin coated at 3000 rpm for 30 s and dried afterwards for 25 min at 145 °C, to form a 70 nm thick hole blocking layer. The photoactive layer was formed by spin coating of carbon-CdSe QDs hybrid materials for 30 s at 800 rpm followed by a 60 s drying step at 1800 rpm. For the cathode, an 80 nm aluminum layer was deposited by thermal evaporation and subsequently annealed at 145 °C for 5 min. Afterwards, they were placed in a glove box under the nitrogen atmosphere without any further encapsulation.

Characterizations

Transmission electron microscope (TEM) observation was performed with JEOL JEM2100F electron microscope (JEOL Ltd., Tokyo, Japan) operated at 200 kV, while the UV–Vis absorption spectra were obtained using a TIDAS 100 J&M diode-array spectrometer (Spectralytics, Aalen, Germany). The current density versus voltage (J–V) characteristics were measured by a computer-controlled Keithley 2400 source meter measurement system under 100 mW/cm^2 illumination with an AM1.5G filter.

Results and Discussion

Effect of acid functionalization

As discussed in introduction section, the utilization of nanocarbon material in hybrid solar cells has obtained attention within the research community. Within this work, a series of experiments have been conducted on the integration of MWCNT into PCPDTBT/CdSe QDs hybrid solar cells. The investigation is focused on the incorporation of CNTs into the photoactive blend of bulk hetero junction (BHJ) hybrid solar cell. However, an inherent hydrophobic characteristic of nanocarbon material limits its application due to difficulties to make stable nanocarbon solutions. As a consequence, nanocarbon solution is usually referred as a suspension. In the context of polymer/QDs hybrid solar cell, there are several difficulties when these nanostructured carbons are incorporated into PCPDTBT/QDs blend systems and hole transport layer material solutions. Precipitation or aggregation of nanocarbon material will affect the internal morphology of the photoactive layer, resulting in poor device performance. In case of hole transport layers, aggregation causes high roughness and poor coverage when they are deposited onto ITO/glass substrates. Therefore, functionalization of nanocarbon materials is considered as an approach to overcome this limitation. Here, nanocarbon functionalization based on acid oxidation and thiolation were performed as described in Section 2.2. The sequence of nanocarbon functionalization is depicted schematically in Fig. 1.

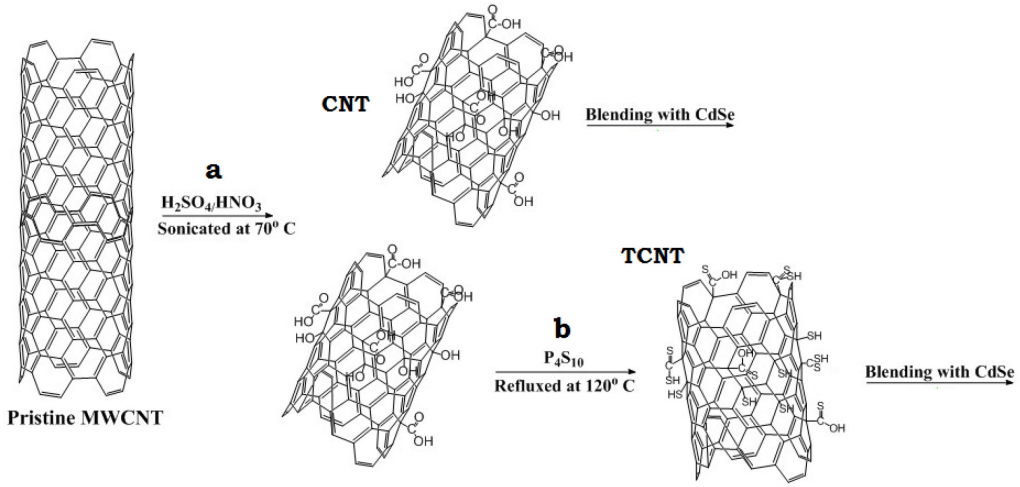

Fig. 1. Schematic illustration of MWCNTs functionalization in this work: (a) conventional acid functionalization (CNT), (b) thiol functionalization, which produced thiolated CNT (TCNT). Both products are blended with CdSe QDs to form hybrid material in the photoactive layer of solar cells. The image was taken from ref [18].

Fig. 2 shows SEM images of as received MWCNTs and MWCNTs after functionalization. It can be seen that as-received MWCNTs showed a huge amount of entangled aggregated tubes and cannot be well dispersed into solvents. Contrary, after acid functionalization, the entanglements of the tubes are significantly reduced, and the tubes have shortened length. As for the polymer/CdSe QDs composite application, separated tubes and shortened length are preferred, because entanglements and longer lengths can make the tubes larger than the overall thickness of the photoactive layer so that electrical short-circuits occurs. In this work, an average length of 357 ± 47 nm has been obtained for functionalized MWCNTs by sonication for 24 hours.

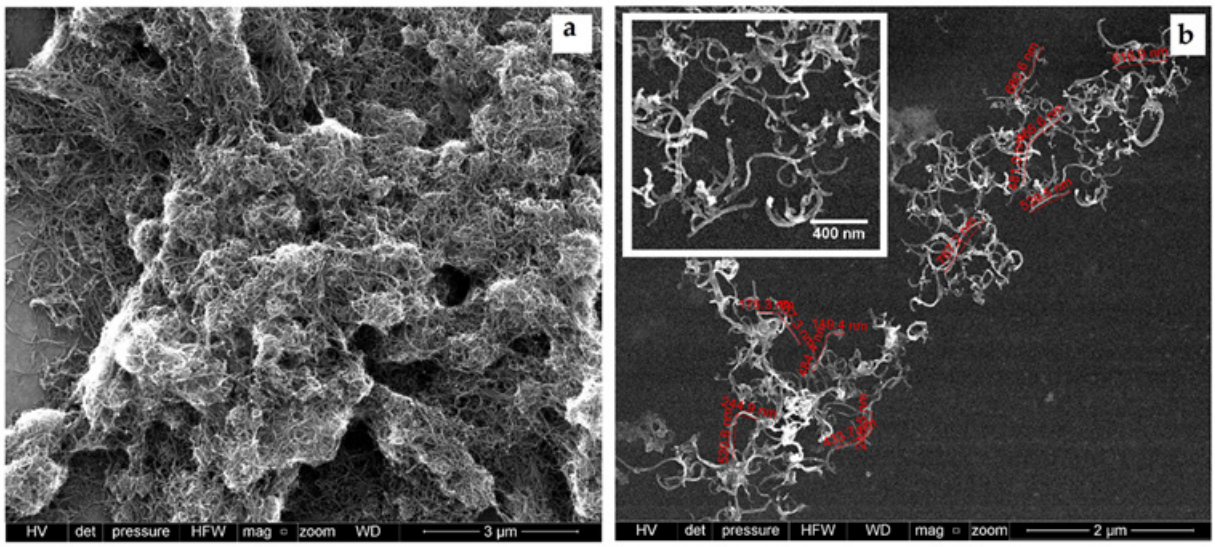

Fig. 2. SEM images of as received MWCNTs (a) and MWCNTs after acid functionalization and sonication for 24 hours (b), the inset image is showing a magnified area from (b), indicating that the length variation ranges changes from > 2µm down to ~ 360 nm.

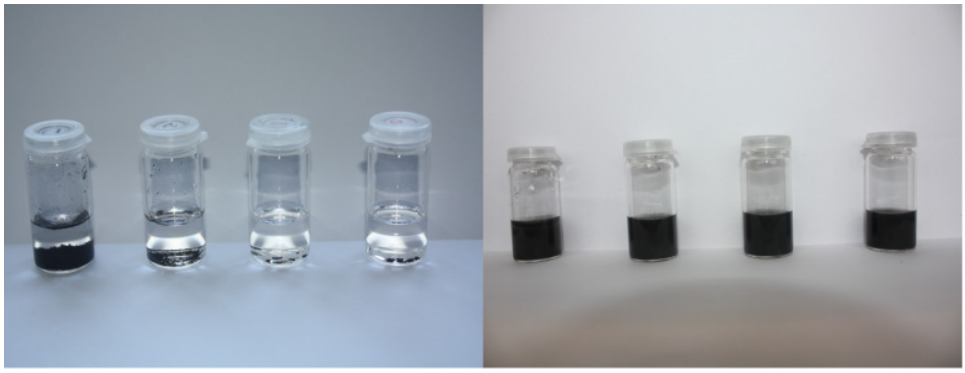

Fig. 3. Photographs of MWCNTs solutions before (left) and after functionalization (right). The concentration was set to 1.2 mg/ml in several solvents, from left to right: in water, DMF, isopropanol, and chloroform.

As shown in Fig. 3, the acid functionalization has been found as an effective way to modify MWCNTs characteristics from hydrophobic to hydrophilic behavior. This is correlated to the introduction of oxygen-containing groups (OCG) after acid functionalization. Before functionalization, MWCNTs cannot be dissolved in solvents, which can be seen clearly the remaining precipitates even after sonication treatment. After functionalization and sonicating for 24 hours, it is observed that MWCNTs became hydrophilic. Water, dimethylformamide (DMF), isopropanol and chloroform are reasonable solvents for functionalized MWCNTs.

Effect of thiol functionalization

The nanocarbon-CdSe QDs hybrid materials were fabricated by a gentle self-assembly decoration process [14]. In order to investigate the hybrid MWCNT-CdSe QDs material, TEM investigation was performed. CdSe QDs with the full width at half maximum (FWHM) value of 24.5 nm, first excitons absorption peak about 631 nm, PL peak at wavelength 645 nm, and average size 6 nm (Fig. 4). For hybrid materials fabrication, a small amount of carbon nanotubes was coincidentally mixed in chlorobenzene by stirring for 10 min. As shown in Fig. 5, it is revealed that the decoration process does not affect shape and size of CdSe QDs. Interestingly, it is observed that MWCNTs which are functionalized with thiol groups show a significantly higher loading with CdSe QDs compared to MWCNTs functionalized with -OH and COOH.

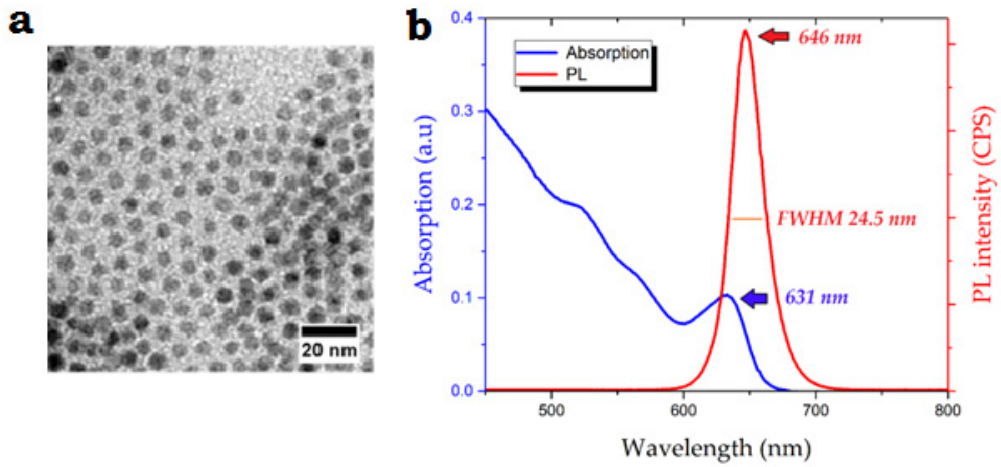

Fig. 4. TEM pictures of CdSe QDs synthesized at 300°C for 30 min (a), UV-Vis absorption and PL spectra for CdSe QDs typically used for the fabrication of hybrid solar cells in this work (b).

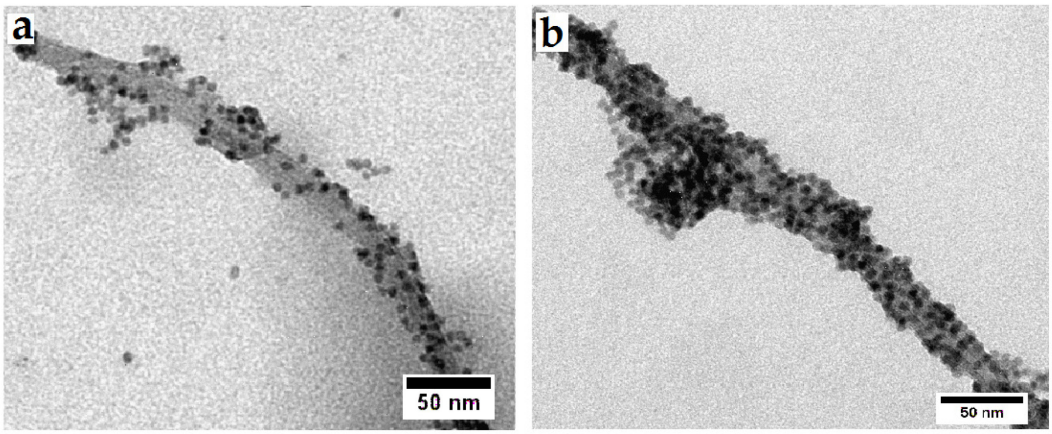

Fig. 5. TEM images of QD nanocarbon hybrid materials: CNT-CdSe QDs (a), TCNT-CdSe QDs (b).

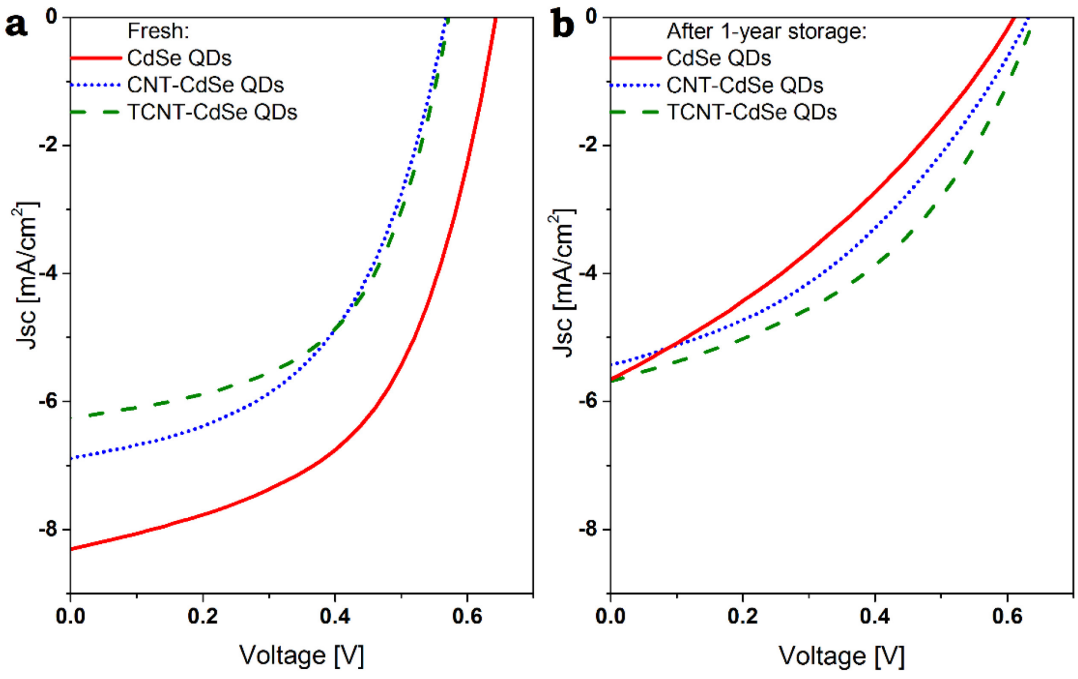

Fig. 6. J–V curves of three different types of hybrid solar based on CdSe QDs, CNT-CdSe QDs, TCNT-CdSe QDs after device preparation (left) and after one-year storage (right).

Table 1. Comparison of best device performances of three different types of hybrid solar cells directly after device preparation (left) and after one-year storage (right).

Cells	Freshly prepared						After one-year storage					
	Voc [V]	Jsc [mA/cm^2]	FF	PCE [%]	Rsh [Ω]	Rs [Ω]	Voc [V]	Jsc [mA/cm^2]	FF	PCE [%]	Rsh [Ωcm^2]	Rs [Ωcm^2]
CdSe QDs	0.64	8.31	0.54	2.81	524.4	11.7	0.63	5.23	0.32	1.06	189.3	44.3
CNT-CdSe QDs	0.56	6.2	0.54	1.85	704.7	13.5	0.64	6.00	0.39	1.48	411.5	32.6
TCNT-CdSe QDs	0.58	5.78	0.56	1.88	794.2	12.0	0.65	5.64	0.43	1.57	414.4	21.3

The results presented in Table 1 show the initial PCE values of differently composed hybrid solar cells, from freshly prepared devices and after they were stored for one year under nitrogen atmosphere. An initial PCE of about 1.9% was reached for CNT-CdSe QDs based and TCNT-CdSe QDs based solar cells respectively. However, CdSe QDs based reference solar cells resulted in initial PCE values of 2.8%. Interestingly, after 1-year storage under nitrogen atmosphere, both of the QDs-nanocarbon hybrid solar cell devices showed a higher PCE compared to CdSe QDs based reference solar cells. CNT-CdSe QDs based cells with 1.57±0.03 %, 1.51±0.17% and 1.48±0.18 % respectively. On the other hand, CdSe QDs based reference solar cells showed the most significant drop in PCE down to 1.06 %. A summary of performance parameters changes of individual solar cells after one-year

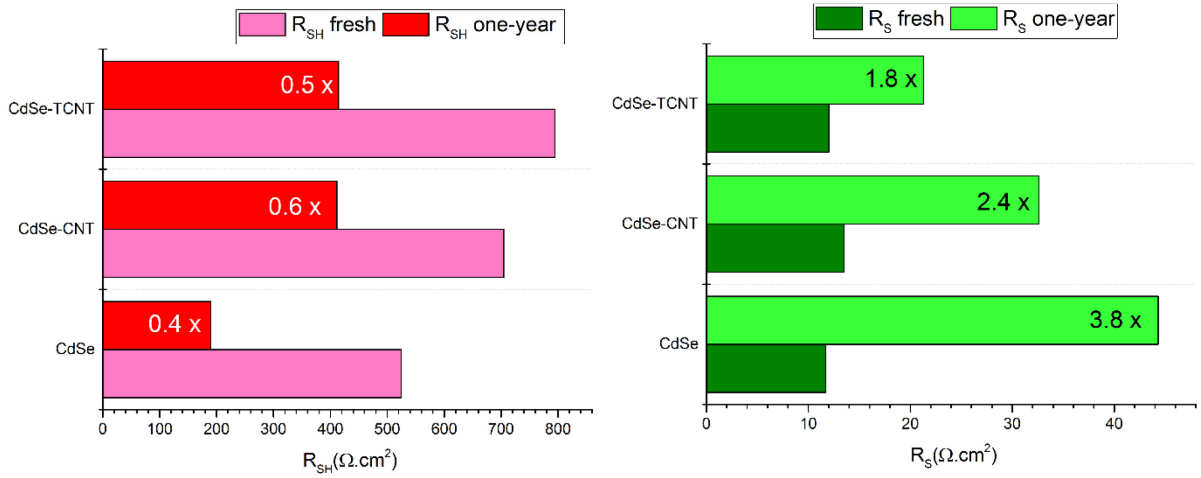

Fig. 7. Summary of absolute values of shunt resistance (Rsh) and series resistance (Rs) for PCPDTBT/CdSe QDs and PCPDTBT/nanocarbon-CdSe QDs hybrid solar cells, and their change (factors compared to fresh devices indicated on the pale bars) after one-year storage.

When searching for the origins of the prior described differences in the immediate and long term solar cell performance, the significantly increased specific shunt resistance of the nanocarbon material containing solar cells is striking (see Figure 6). The relatively lower R_{sh} of the CNT-CdSe QDs containing solar cells compared to the thiolated nanocarbon materials, points towards a higher loading of CdSe QDs in the active layer (Figure 5.18) [19]. The initial values of the specific series resistances (R_s) are fairly similar for all three solar cell types. However, the picture drastically changes when looking at the R_s values of degraded solar cells. Then, the solar cells containing the thiolated nanocarbon materials show only an increase of R_s by the factor of about 2, while CNT containing solar cells show a 2.4-fold increase, and the nanocarbon-free solar cells exhibits an increase even a 3.8-fold of R_s. The series resistance is composed of a contact resistances and a bulk resistance part– with the latter being dominant in organic BHJ solar cells[20]. Therefore, by considering that the absolute increase of R_s due to contact resistances is similar for all four solar cell types, one can conclude that the predominant effect observed is caused by the change of the bulk resistance.

Summary

In conclusion, we observed that the incorporation of MWCNTs helps to preserve the low bulk resistance in hybrid BHJ solar cells on the long term, and that this preservation effect is strongest for the thiolated nanocarbon-CdSe QDs containing hybrid solar cells. The total of loss of 62% in PCE was recorded for CdSe QDs based solar cells, whereas CNT-CdSe QDs and TCNT-CdSe QDs solar cells exhibited a loss in PCE of only about 20% and 16% respectively. It can be assumed that this improved preservation is resulted from a higher stability of the initial active layer nanomorphology for the nanocarbon/CdSe QDs based hybrid solar cells. Also, a recent study reports that carbon material like graphene provides surface passivation for CdSe QDs and hence lowers oxidation and aging processes of CdSe QDs [21]. This might explain our observation that the solar cells containing thiolated nanocarbon materials exhibit the best long-term stability due to the covalent binding and thus surface passivation of CdSe QDs.

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